CARBON FOOTPRINTING

Factors driving refinery CO₂ intensity, with allocation into products

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Received: 3 September 2009 / Accepted: 1 June 2010 / Published online: 23 June 2010 © The Author(s) 2010. This article is published with open access at Springerlink.com

Abstract

Background and scope Attempts to develop adequate allocation methods for CO₂ emissions from petroleum products have been reported in the literature. The common features in those studies are the use of energy, mass, and/or market prices as parameters to allocate the emissions to individual products. The crude barrel is changing, as are refinery complexities and the severity of conversion to gasoline or diesel leading to changes in the emissions intensity of refining. This paper estimates the consequences for CO₂ emissions at refineries of allowing these parameters to vary.

Materials and methods A detailed model of a typical refinery was used to determine CO₂ emissions as a function of key operational parameters. Once that functionality was determined, an allocation scheme was developed which calculated CO₂ intensity of the various products consistent with the actual refinery CO₂ functionality.

Results The results reveal that the most important factor driving the refinery energy requirement is the H₂ content of the products in relation to the H₂ content of the crude. Refinery energy use is increased either by heavier crude or

Responsible editor: Matthias Finkbeiner

Electronic supplementary material The online version of this article (doi:10.1007/s11367-010-0204-3) contains supplementary material, which is available to authorized users.

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R. Quiceno-Gonzalez (: X. Riera-Palou · A. Harrison Shell Global Solutions, Shell Technology Centre, Thornton, PO Box 1, Chester CH1 3SH, UK e-mail: raul.quiceno@shell.com by increasing the conversion of residual products into transportation fuels. It was observed that the total refinery emissions did not change as refinery shifted from gasoline to diesel production.

Discussion The energy allocation method fails to properly allocate the refinery emissions associated with H₂ production. It can be concluded that the reformer from a refinery energy and CO₂ emissions standpoint is an energy/CO₂-equalizing device, shifting energy/CO₂ from gasoline into distillates. A modified allocation method is proposed, including a hydrogen transfer term, which would give results consistent with the refinery behavior.

Conclusions The results indicate that the refinery CO_2 emissions are not affected by the ratio of gasoline to distillate production. The most important factors driving the CO_2 emissions are the refinery configuration (crude heaviness and residual upgrading) which link to the refinery H_2 requirement. Using the H_2 -energy equivalent allocation proposed in this study provides a more reliable method to correctly allocate CO_2 emissions to products in a refinery in a transparent way, which follows the ISO recommendations of cause-effect and physical relationship between emissions and products.

Recommendations and perspectives Regulatory activity should recognize that there is no functional relationship between refinery CO₂ emissions and the production ratio of gasoline, jet, and diesel, and adopt a methodology which more accurately mirrors actual refinery behavior.

Keywords CO_2 allocation methods · Carbon footprint · Crude oil refining CO_2 emissions · Diesel production · Energy-consuming products · Gasoline production · H_2 effects on refinery CO_2 · Life cycle assessment · Refining emissions



1 Background, aim, and scope

Policy makers and regulators are seeking to impose greenhouse gases (GHG) performance standards on fuel lifecycles, e.g., California's Low Carbon Fuel Standard (LCFS 2007) and the European Union's Fuels Quality and Renewables Directives (COD 2008). The common feature of these regulations is that fuel providers will be required to track the lifecycle (i.e., well to wheels) GHG emissions intensity of their products, measured per unit of fuel energy, and reduce this value over time. Furthermore, the US Environmental Protection Agency is assessing fuel lifecycle GHG emissions intensities for the Energy Information and Security Act. Models describing emissions in the fuel lifecycle, which were designed to meet academic scenario forecasting needs, now have to be redesigned to suit regulatory applications, with the associated legal and commercial implications.

Crude oil based transport fuels are produced concurrently with other fuel and non-fuel products. Consequently, overall CO₂ emissions generated by the refining process can be distributed between the individual products through "allocation" rules. Historically, such rules have reflected the scope and goals of the study, the modeler's understanding of the process, the available data and end-use options for the products because there is no theoretical basis for choosing one allocation scheme over another. When some refining products are regulated on their carbon content but not others, it is important to ensure that the allocation rules reflect the actual climate impacts of the regulated products as fairly as possible, whilst at the same time, minimizing incentives to transfer responsibility for the impacts onto unregulated products.

The International Standard Organization (ISO) guidelines for lifecycle assessment (LCA) recommend that allocation should be avoided wherever possible, but where this is not possible, the allocation should reflect quantitatively or qualitatively how environmental impact changes with product yield. Some authors have suggested options to refine the ISO methodology and the accuracy of the results (Ekvall and Finnveden 2001). Ultimately, however, it is left to the LCA practitioner to decide how to follow these recommendations. As a result, the literature contains several different estimates for the carbon intensity of gasoline and diesel production even for similar systems (Furuholt 1995).

The problems faced in solving the issue of allocation in multi-product systems are fairly well known, and they have been extensively discussed in the literature (Azapagic and Clift 1999; Ekvall 1999; Babusiaux 2003; Ekvall and Weidema 2004). Different accounting schemes have been proposed to assign emissions to the plant products typically based on mass, energy, or market value shares of products. More recently, linear programming (LP) models, which have

a long tradition in the refining industry (Charnes et al. 1952; Griffin 1972; Palmer et al. 1984), have been extended to calculate CO₂ emissions, and to assign individual product contributions to the CO₂ emissions in refineries through a marginal approach (Azapagic and Clift 1999; Babusiaux 2003). These models follow a similar logic to that used in assigning costs to refinery products: global CO₂ emissions are allocated to products based on the incremental CO₂ emissions generated in manufacturing an additional volume of the products. The resulting product CO₂ intensities are sometimes, but not always, different from those estimated under traditional mass/energy allocation schemes. Neither type of method is superior; but each has its domain of validity and applicability.

Furuholt (1995) compared the energy consumption and pollutant emissions in the production and end use of regular gasoline, gasoline with MTBE, and diesel. Energy consumption and emissions were tracked through the production chain and emissions were allocated to products based on their energy content. The results were highly sensitive to the product specifications, and it was predicted that emissions from diesel production were significantly lower than those from production of gasoline as a consequence of "diesel's lower process energy requirement".

Wang and coworkers (Wang et al. 2004) compared the impact of different allocation rules applied at the process unit level in a US refinery. They used as an archetype refinery a detailed quantitative process-step model of petroleum refining developed in the late 1970s at Drexel University (Brown et al. 1996). The mass and energy balances at each process step of this archetype constitute the reference process-step model for petroleum refineries (Ozalp and Hyman 2007). Wang et al. (2004) compared the use of mass, energy content, and market value share of final and intermediate petroleum products as allocation weight factors at the process unit and the refinery levels. They defined product energy intensities for major refinery products (defined as the fraction of process energy invested in producing a particular product relative to its weight factor), and concluded that wherever possible, energy use allocation should be made at the lowest sub-process level (Wang et al. 2004). They found diesel production to be less energy intensive than gasoline production in each of the allocation weighting methods used (mass/energy/market value; refinery/process unit level) as predicted by Furuholt (Furuholt 1995).

Tehrani (Tehrani 2007) used an LP model to study the CO₂ emissions allocation problem for a European price-taking refinery operating in a cost-minimizing environment. It was assumed that the refiner's objective is to satisfy a petroleum production target at the minimum cost and subject to constraints of prevailing technology, commodity prices, input availabilities, oil product demand, capacity



constraints, material balance, and product quality. Tehrani concluded that emissions could be allocated among products using "average allocation" coefficients containing two contributions, a direct one, which is its marginal $\rm CO_2$ intensity, and an indirect contribution, which depends upon the production elasticity of unit processes and is calculated at the LP optimal solution ex-post. This approach was later used (Tehrani and Saint-Antonin 2007) to assess the impact of reducing sulfur in European automotive fuels on the refining emissions intensity of gasoline and diesel. It was shown that, contrary to prior results (Furuholt 1995; Wang et al. 2004), gasoline refining could be less emissions intensive than diesel refining.

Pierru (2007) used an alternative LP optimization function including operating costs and cost associated with the refinery's CO_2 emissions to calculate the marginal emissions (in accordance with economic theory) from the various refinery products. The study highlights the impact of constraints such as demand, refinery capacity, and raw material supply on the CO_2 emissions originated at refineries. It was concluded that contrary to traditional LCA studies, diesel has a higher marginal contribution to refinery emissions than gasoline.

The common features in the above studies, notwithstanding the different approaches, constraints, and results are: single-fixed refinery configuration, fixed unit throughput capacities and fixed crude diet.

The crude barrel is changing, as are fuel specifications, and these will lead to changes in refining emissions intensities. In this paper, we therefore focus on the consequences of varying the crude diet, the severity of conversion to gasoline or diesel, and the complexity of the refinery. The critical element is the hydrogen requirement, since its production and consumption is highly carbon intensive. A detailed analysis of the hydrogen flow through the refinery is carried out at each refinery unit, in order to establish the carbon footprint of products. Based on this work, we propose a more realistic way to estimate the energy and emissions intensities of refinery products.

2 Materials and methods

The refinery simulation model is a case study model used by Shell to select crude type, determine refinery products, and calculate refinery economics for major investment decisions. Shell has high confidence in its accuracy.

Yield representations reflect crude boiling curve, hydrogen content, aromaticity, sulfur, nitrogen, and other relevant parameters associated with the refinery crude diet. Several of those terms (boiling curve, hydrogen content, and aromaticity) are at least partially covariant with crude density (API gravity), but it is more accurate to handle

them individually. Processing severity can be adjusted by distributing feeds differently within the refinery flow matrix, by changing reactor severity of individual processes, and by varying fractionator cut points. Energy consumption was determined by summing feed-rate-based consumption factors for each process unit (some of which are functions of that unit's severity). Feed gas and fuel gas energy for H₂ manufacture are included. Hydrogen balance is maintained throughout the model, meaning the hydrogen contained in all feeds equals the hydrogen contained in all products from each unit. Relatively few refinery models have that feature; meaning that their prediction of how much hydrogen is required from the hydrogen plant is less reliable. Since hydrogen plant size is critical to refinery CO₂ emissions, this is an important advantage for this study.

Specific process units included were: crude distillation, delayed coking, fluid catalytic cracking, hydrocracking, naphtha reforming, alkylation, hydrotreating (naphtha, distillates, fluid catalytic cracking (FCC) feed), hydrogen manufacture, sulfur recovery, and various other enabling process units typically included in a refinery (the refinery flow chart is available as Online Resource 1).

Product specifications were gasoline was US reformulated gasoline in a typical grade mix of regular to premium. Diesel was US ultra low sulfur diesel. Jet was Jet-A, and in cases where produced, residual was US Gulf Coast high sulfur Fuel Oil #6. Naphtha from the catalytic cracker was hydrotreated such that gasoline pool sulfur was 25 ppm. Jet smoke and diesel cetane number using a normal severity distillate hydrotreating unit were inside fuel specifications for all except two of the crudes analyzed. This was ignored because real refineries have some scope to blend streams to meet specifications, and if not, the refinery would run a blend of crude rather than neat crude. The three low value residual streams (Cat slurry, Fuel Oil #6 and Coker Coke) were summed into a single product class called residual/ coke. To summarize, the product streams considered were liquefied petroleum gas (LPG), gasoline, distillate (including gasoil and kerosene), and residual/coke.

It was considered critical that the results from the allocation methods and the results from the model runs be consistent. In other words, if the refinery runs showed no difference in total refinery CO_2 emissions as the gasoline to diesel ratio was varied, then the CO_2 intensity of those two fuels should be the same.

3 Results

Three issues were studied explicitly: crude heaviness (fraction boiling >1,000°F/540°C), production ratio of gasoline to distillates, and whether the refinery processed



its 1,000°F/540°C+vacuum resid in a delayed coker or blended it to Fuel Oil no. 6. Issues such as ratio of FCC to hydrocracking capacity, the type of benzene production controls employed, whether C_5/C_6 isomerization is employed, in cases with residue reduction, whether the residue reduction unit was a delayed coker, other type of coker, or other type of unit such as LC-Finer or resid hydrotreater, and any number of similar configurational issues could perturb the numerical results. Pair cases simulations (base Vs base + δ), where δ refers to a perturbation on the variable under analysis were run to assess the robustness of the results and to ensure that they did not have a material impact on the conclusion reached through the study

3.1 Matrix of cases

Crude heaviness was studied by selecting six crudes with quantity of vacuum bottoms (>550°C) ranging from 10% to 35% (lightest Brent, heaviest Maya). Production ratio of gasoline to distillate was varied by shifting from gasoline to distillate mode which means lowering FCC and HCU reactor severities, and changing cut points at crude unit, cat cracker, and hydrocracker. Cut points were shifted on both ends, lowering naphtha/distillate cut point and raising distillate to FCC feed cut point. Production of resid was changed by shutting down the coker, and sending coker feed to #6 oil blending instead. Case names of these conditions were captured in a four character code. The first character was either K or 6, representing a coker case or a case that produced #6 residual fuel oil. The second and third characters were C for crude, and a number, meaning the crude heaviness choices from 1 to 6. The final case was H or L meaning high or low severity to gasoline. So for example, KC3L was a coker case on crude 3, with low severity to gasoline. Or case 6C5H was a #6 fuel oil case on crude 5 with high severity to gasoline. In all, the refinery was run in four modes (high/low gasoline, with/without coker) with six different crudes to produce a matrix of 24 data points. For each case, refinery yields and fuel/CO₂ data were generated. Refinery yields data are available as Online Resource 2. The fuel/CO₂ data were split by process needs and H₂ generation needs.

One aspect of these runs was different from typical model running strategy. In most model studies, one must stay within capacity constraints of the various process units. But in this study, there are wide variations of crude heaviness, which would far exceed the acceptable flow rate variations for individual units in any given refinery. So individual process unit throughputs were allowed to vary as needed, such that each intermediate stream in the refinery headed to its normal consuming unit. Had that not been done, the results would have been strongly and inappropri-

ately biased by internal constraints. This way, it was as though each case had a custom tailored refinery to allow ideal flows for that case.

3.2 Numerical results

Consider the results as being four blocks of data, with six cases in each block. The four blocks are with/without coker (i.e., high/low resid production), high/low conversion to gasoline, and within each of those four blocks, the six crudes of varying heaviness. These four blocks are shown in Fig. 1.

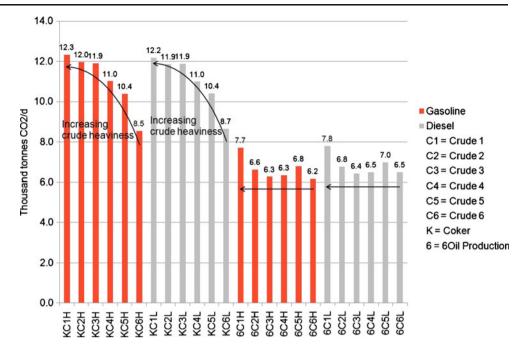
Comparing the left two with the right two blocks on Fig. 1 shows that adding the coker to eliminate the no. 6 fuel oil production clearly increases CO₂ emissions for all case pairs involving that switch. Not only does the coker consume energy in its own right, it upgrades a low hydrogen content product stream (no. 6 fuel oil). This in turn requires the refinery to run other cracking and hydrogen consuming units harder to boost the hydrogen content up from resid hydrogen levels (because resid is no longer being produced) to mogas/jet/diesel hydrogen levels (because those higher hydrogen content products are being produced instead of resid).

Changing the severity and cut points to vary the ratio of gasoline to distillate has very little effect in any of the cases in any of the case pairs where that change was made (see Fig. 1). At first, this might seem illogical because to go to lower boiling point gasoline, the level of cracking needed is harder, and that would seem to require more energy. The counter-balancing point is H2 content. In gasoline production, aromatics are favored due to higher octane ratings and this is where the reformer's H₂ production comes into play. To make more gasoline, reformer feed rate increases and as reformers also produce H₂, the amount of H₂ that must be made in the CO₂ intensive H₂ plant decreases, and on balance, the overall CO2 emissions do not change very much. In contrast, for jet and diesel production, paraffins are favored. In fact, despite its lower boiling point, H₂ content of gasoline is similar to jet and diesel.

What happens with crude heaviness depends on whether there is a coker (or other residue reduction unit). The left two blocks of Fig. 1 show that if there is a coker to eliminate resid, heavier crude needs a bigger coker, which consumes more energy, and demands more hydrogen consumption in downstream units, thus increasing CO₂ emissions (from running the hydrogen plant at a higher rate). The right two blocks of Fig. 1 show that without a coker, the refinery produces resid as a product, so CO₂ emissions do not change very much with crude heaviness. However, the heavier crude makes more resid in comparison to transportation fuel, and that is an indirect CO₂ penalty because more carbon intensive resid product fuels



Fig. 1 Overall refinery CO₂ emissions



are being produced. Note that this issue of with/without coker, or higher/lower residual fuel production is sometimes referred to as refinery complexity. The coker (or other residue reduction unit) adds complexity not only because it is an added large process unit, but also because products from residue reduction units are low quality, which requires other units within the refinery to be larger and higher severity in order to upgrade them.

The fact that CO₂ emissions are practically independent of light product ratio shifts from gasoline to diesel shows that the CO₂ emissions at refinery level are not driven by the differential energy demands of these products, but by other factors: crude heaviness and whether the refinery has a coker to eliminate production of residual fuel. A third route to CO₂ emissions reductions is energy conservation; all routes can be influenced by external issues such as crude availability, product demands, and prices.

4 Discussion

It was shown in Section 3 that two operational routes significantly lowered total refinery CO_2 emissions. The production ratio of gasoline to diesel fuel was not one of those factors, because interaction of some non-obvious hydrogen issues equalizes the total refinery CO_2 emissions from production of gasoline and diesel fuel. The hydrogen balance at the refinery, together with the results from tracking products through process units in terms of the energy consumed during their production and their associated CO_2 emissions are described in the next sections. Both results are used to develop an allocation strategy consistent with refinery CO_2 emissions behavior.

4.1 Hydrogen balance

One of the most critical factors in refining is hydrogen balance. This is not just hydrogen balance in the sense of flows of elemental hydrogen gas as a processing stream but also the hydrogen content of feeds and products. Since crude oil is generally low in hydrogen content, and refined products (except for residual fuel and coke) are high in hydrogen content, refineries are forced to produce the additional H₂ that satisfies their needs in a process that its intrinsically highly CO₂ emissions intensive.

Carrying this hydrogen issue a bit further, if the crude has less hydrogen coming in (most common explanation being that it is heavier), or the products have more hydrogen going out (most common explanation being more transportation fuel with correspondingly less residual fuel), the refinery energy consumption will invariably be higher. While it is true that there are many possible routes and configurations of refineries (for example, cat cracking versus hydrocracking), all refineries by all routes are bound by this hydrogen balance issue. The exact configuration of a refinery can cause minor variations in energy/CO₂, but the simple difference in hydrogen content between crude coming in and products going out are by far, the controlling factor.

In a typical refinery, roughly half of the H_2 is produced as a by-product from the catalytic reformer (and in the few refineries that have them, from the olefins plant) (NETL 2008). Most allocation schemes allocate the energy and CO_2 from the "on purpose" H_2 plant properly, but they ignore the impact of the reformer H_2 , and if applicable, from the H_2 produced at the olefins plant. Ignoring the reformer H_2 production means that the H_2 consuming units



get a substantial part of their H_2 requirements as a CO_2 -free stream, and also that the reformer is not credited for the large CO_2 avoidance associated with its H_2 production and the displaced H_2 from the "on purpose" H_2 plant.

Production of gaseous H_2 in "on purpose" H_2 plants can be typically characterized by a well to tank footprint of circa 108 gCO₂e/MJ (GREET 2008). By comparison, the gasoline footprint is around 90 gCO₂e/MJ in GREET. This highlights the importance of correctly accounting for CO₂ emissions in processes involving hydrogen production.

If one looks at what drives hydrogen content of crude, it is mostly the heaviness, i.e., how much boils above $1,000^{\circ}\text{F}/540^{\circ}\text{C}$. There is a modest added effect for whether the crude is of naphthenic or paraffinic character, but heaviness is more important. One would expect that the heavier the crude, and thus the less hydrogen that the crude contains, the higher the energy requirement and CO_2 intensity of the refinery.

On the product side, gasoline, jet, and diesel have roughly equivalent hydrogen content: For the main transport fuels¹, the C/H ratio would range for gasoline (EN220) ~1.7-1.9, for diesel (EN590) ~1.7-1.9 and for jet A-1 $(AFQRJOS^2) \sim 1.7-1.9$. The mass ratio (carbon to hydrogen) estimated for these fuels range between 6.3 and 6.9 m/m for all of them (see footnote 1). It might seem logical to think that gasoline should have more hydrogen than jet or diesel because it has a lower boiling temperature range, and hydrogen content is normally higher as boiling point gets lower. But actually, because quality issues force a bias toward aromatic species for gasoline to maintain its octane rating, while at the same time there is an opposite bias toward paraffinic content for jet and diesel to maintain their smoke point and cetane ratings things balance out in such a way that the main transportation fuels are similar in hydrogen content, and thus should be similar in their CO₂ emissions intensity.

LPG (generally C₃ and C₄ molecules) contains more hydrogen than gasoline, jet, and diesel, so should have higher CO₂ intensity. Some might think LPG should be low CO₂ intensity since much of it comes from simple fractionators. But LPG is not an "on-purpose" product, it is a byproduct. If more LPG were made by choosing catalysts that did more overcracking, the LPG would carry away more hydrogen in the product, requiring more refining and hydrogen manufacturing energy.

By contrast to high hydrogen LPG, residual fuel oil has very low hydrogen content. Resid can either be produced by the refinery as a product, or cracked in a resid cracking

² Join Inspection Group, Products Specifications. Aviation Fuel Quality Requirements for Jointly Operated Systems (AFQRJOS). Issue 22–28 June 2007



unit such as a coker. Coking is energy intensive, not only because of the coker itself, but also because the coker makes hydrogen deficient products which need extra hydrogen to be added in subsequent refining steps. Allowing the resid to go out as residual product rather than cracking it to lighter products saves large amounts of energy, thus making resid a very low energy product.

While not explicitly studied in the model runs described in this paper, other factors can influence refinery CO₂ emissions. One example has already been mentioned, namely, energy conservation which would lower CO₂ emissions. Others would include product specification changes such as lower sulfur or lower aromatics, which would raise CO₂ emissions. And finally, going to production ratios of products outside "normal ranges" could negate the conclusion that all of the light transportation fuels have "roughly equal" CO2 emissions. If a refinery is forced to make more of a particular fuel than can be accommodated within "natural refinery flexibility" (such as very high diesel production, with very low gasoline production), CO₂ emissions would clearly increase. Variations in production ratios modeled in this paper were all within normal ranges of refinery flexibility, with an average swing between gasoline and diesel for high to low gasoline cases of around 4% on crude, and ranged between 2% and 6% depending on crude type and refinery configuration.

Subject to these caveats, we might expect that the refinery production of CO₂ (i.e., consumption of fuel, including the fuel needed to manufacture hydrogen) to produce gasoline, jet, and diesel should be roughly equal. Because refinery energy is mostly proportional to product versus feed hydrogen content, and the hydrogen content of gasoline, jet, and diesel products are similar. Using this same logic, LPG should be higher in CO2 intensity and bunker-type residual fuel lower. CO₂ emission and energy consumption will be higher for heavier crudes than light, and slightly higher for naphthenic than for paraffinic crudes. Other factors should not influence refinery energy consumption as shown by the refinery model runs described in Section 3. Hydrogen content of the various feed and product streams is the main driver of refinery CO₂ intensity critically important in developing a proper allocation scheme.

4.2 Allocation approaches

Many allocation methods have concluded that refining to gasoline is much more energy intensive than distillate, which is inconsistent with the findings in the previous section, where varying gasoline/distillate ratio did not have much effect on CO₂ emissions. To understand why, a typical allocation approach was applied to the data from Section 3.

¹ Shell Internal data

The energy consumptions of the individual process units from the 24 runs in Section 3 were distributed into products according to process unit yields from those runs. For example, if a given unit consumed 10 units of energy, and its yields were 40% gasoline, 40% distillate 10% LPG, and 10% resid; its 10 units of energy would be allocated 4, 4, 1, 1 to those products. For the hydrogen plant, energy was distributed to the individual units according to the relative hydrogen consumption of that unit and from there byproduct, as with the normal fuel. Using this approach, gasoline was approaching a factor of two times more energy intense than distillate. But this handles hydrogen incorrectly.

In the above scheme, the fuel and feed gas associated with the hydrogen plant is allocated to the hydrogenconsuming units on the basis of their relative hydrogen consumptions, and from there to products. However, only about half of the refinery's hydrogen comes from the hydrogen plant. The remaining half comes from the catalytic reformer, which is totally associated with gasoline production. Recall from Section 4.1 that gasoline is biased toward aromatics for quality purposes (i.e., octane rating), and the reformer is the process step that gives this bias. If the refinery makes less gasoline, it would have a smaller reformer, which would make less hydrogen, which would then require a larger hydrogen plant, which would consume more energy. So the reformer, from a refinery energy and CO₂ emissions standpoint, is an energy/CO₂ equalizing device, shifting energy/CO₂ from gasoline into distillates.

If the allocation scheme does not recognize this hydrogen-equalizing feature of catalytic reforming, it will conclude that gasoline has greater CO_2 and energy intensity than jet or diesel. But once the hydrogen production of the reformer is included in the allocation, the allocation will correctly show essentially equivalent energy intensity for gasoline, jet, and diesel. Note that this decision on how to allocate is not arbitrary. Without the reformer hydrogen correction, the allocation does not match actual refinery behavior, while with it, it does. So refinery reality, not arbitrary shifting, is being used to guide the allocation method.

There are various algebraic ways of including the reformer hydrogen production in the allocation scheme. The one chosen counts the energy equivalent of hydrogen as a credit/debit to each unit (credit to H₂ producing units, debit to consuming units), and does not count the hydrogen plant (because it is implicitly counted by debiting the consuming units for the energy equivalent of their hydrogen consumption). Using this technique, the consuming units pay the CO₂ penalty for all of their hydrogen, not just the fraction of hydrogen coming from the hydrogen plant. With this technique, the CO₂ intensity of gasoline versus distillate equals out, which agrees with the observed refinery behavior, which is that refinery energy consump-

tion does not change as gasoline to distillate ratio changes. If gasoline was more energy intensive than distillate, that would not be true.

4.3 Allocation results

The behavior described in Section 4.2 is shown quantitatively in Figs. 2 and 3. Starting with Fig. 2, which has only the coker cases, the right hand side has the results from the simple allocation without hydrogen correction. It shows much greater CO₂ intensity for gasoline using that approach. The left side of the figure includes the hydrogen correction, and gasoline is similar to distillate in CO2 intensity. There is a slope in both blocks, with heavier crudes showing more energy consumption. This is the same slope as was seen in the left two blocks of Fig. 1 (discussed in Section 3), and is caused by the fact that heavier crudes require more coking. Fig. 3 is similar to Fig. 2, except that it has the #6 oil cases rather than the coker cases. It shows most of the same trends, for the same reasons, as Fig. 2. The only differences are that there is essentially no bias for crude heaviness, and the overall levels are lower than in Fig. 2. These differences also link back to Fig. 1, where the #6 oil cases had similar CO₂ emissions regardless of crude heaviness, and had lower CO2 emissions than the coker cases. The slight slope with regard to crude heaviness in Fig. 3 is caused by two things: (1) the highly paraffinic far right crude is slightly low, while the highly naphthenic far left crude is slightly high, and (2) there is an eye-catching slope in Fig. 3 with regard to LPG, but LPG is a small flow, explained by other factors (see next paragraph). So concentrating on the gasoline and distillate, Fig. 3 is essentially flat with regard to crude heaviness. But while CO₂ emissions are flat, there is an indirect, heavy crude CO₂ penalty in the Fig. 3 cases because with no coker, more carbon-rich resid product leaves the refinery as the crude gets heavier.

Looking at the corrected distributions, a few other observations can be made. First, resid product has very low CO₂ intensity as no energy has been spent cracking it or adding hydrogen to it. Second, LPG has very high CO₂ intensity. While a very small amount of LPG is contained in crude oil, and is thus produced with low CO₂ intensity through simple fractionation, most of it is produced by cracking in the high CO₂ intensity cracking units. Indeed, the LPG CO₂ intensity increases with heavier crude. As crude gets heavier, the cracking units get larger, so a larger proportion of LPG comes from cracking rather than simple fractionation. And if a refinery were forced to make even more LPG on purpose by over-cracking, the LPG energy intensity would go up even further. So LPG over and above the very small quantity contained in crude oil should not be regarded as a low energy intensity product.



Fig. 2 Comparison between allocation methods for coker cases

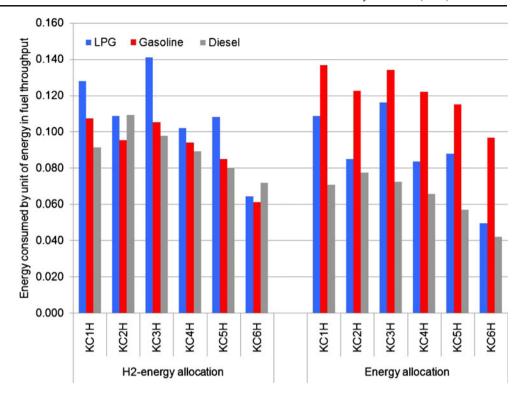
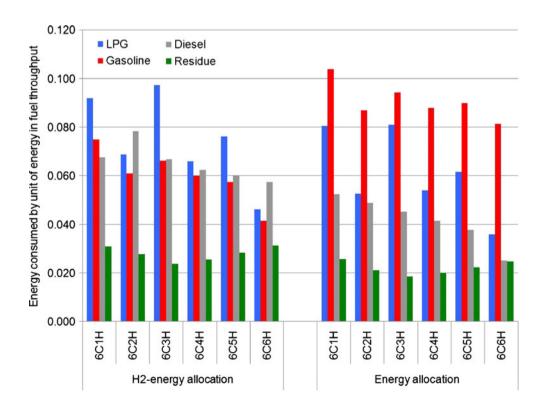


Fig. 3 Comparison between allocation methods for six oil cases





5 Conclusions

Total refinery CO₂ emissions are not strongly affected by ratio of gasoline to distillate product.

To agree with the above conclusion, an allocation scheme cannot conclude that gasoline is more CO_2 emissions intensive than distillate. To avoid that result, the allocation scheme must distribute energy into the various refinery products in a way that takes reformer hydrogen into account.

Refinery CO_2 emissions increase as it produces more transportation fuel and correspondingly less resid product. Operationally, this means that the refinery has a coker or other residue reduction unit, or said in another way, it is more complex.

In a complex refinery with a coker (or other residue reduction unit), making little or no residual fuel product, refinery CO_2 intensity is increased by running heavier crude. In a refinery that does not have a coker, and thus produces substantial quantities of residual fuel product, crude heaviness has little impact on total CO_2 emissions.

Refineries cannot vary LPG production by much, but if forced to make more LPG, total CO₂ emissions would increase. There is no way to make less LPG, it is minimized already.

While not studied explicitly in this paper, it should be self-evident that total refinery CO₂ emissions are also affected by degree of energy conservation excellence (i.e., capital equipment for energy conservation purposes) and by product specifications such as sulfur and aromatics.

6 Recommendations and perspectives

The conclusions on what impacts CO₂ intensity would seem to have obvious implications for regulatory methodologies. But there are a few added considerations that may not be immediately obvious from the conclusions themselves.

Allocation of refinery CO₂ emissions to individual products which does not stick to the technical reality is, by its very nature, rather arbitrary. This can be seen from the fact that using or not using the hydrogen corrections described in this paper has a dramatic impact on the allocation results. That arbitrariness should caution one against taking allocation results too literally. But if one insists on doing an allocation, at least it should be consistent with observed refinery behavior. The refinery behavior is that CO₂ emissions do not change very much with production ratio of gasoline to distillate. Thus, any allocation scheme which shows CO₂ intensities of gasoline and distillate are substantially different must be seen with caution, and special care should be put into understanding

the handling of internal flows, the technical premises assumed, and how they align with the scope and goals of the LCA. Only with the understanding of the full context it is possible to conclude about the results and their implications.

The conclusion that CO_2 can be reduced by making more residual product in less complex refineries without cokers must be tempered with recognition that: (1) it would also lead to a carbon-rich stream (the resid) leaving the refinery; (2) refinery configurations and decision on make yield are driven many other external factors, for example, supply/demand balance of different products; and (3) well-to-wheels or life cycle effect should be considered in determining CO_2 reduction.

Similarly, the conclusion that CO_2 can be reduced by running lighter crude must be tempered with the realization that world crude demand is expected to continue to increase while world supply of light crude is limited [LBST 2007; EIA 2009]. Given that, it is likely that world demand for heavier crudes will continue to increase in the near future to meet consumer demand for transportation fuels.

Areas for further development This paper has not thoroughly handled jet versus diesel, grouping them instead as combined "distillate" fuel. If done simplistically, jet would show as being less energy intensive, because most jet comes via the crude unit and a low severity hydrotreater. But in similar fashion to LPG, if forced to make added jet, a refinery would need to include hydrocracked jet, and that is very energy intensive, often requiring a post-saturation step. Allocation methods could be developed to handle that complication, but that was thought to be beyond the scope of this paper. Instead, the simplifying step of combining jet and diesel into "distillate fuel" was adopted. However, this simplification does not undermine the conclusion that gasoline and diesel have similar overall refinery CO₂ emissions intensity. Simplistically, if jet is viewed as low CO₂ intensity, the algebra of the situation would force the intensity of diesel to be higher to balance. Thus, it does not offer a path back to the conclusion that gasoline is worse than diesel.

It is also acknowledged that precise refinery configuration or exact fuels specifications have not been studied in this study. Some runs were conducted to verify that those issues are far less important than the factors described herein, but it cannot be concluded that their effect is zero. In fact, the next phase of our work will be to study those issues more closely to determine which, if any, of such effects are non-trivial.

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